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# TREATMENT OF CARBIDE SLUDGE FROM AN ACETYLENE PRODUCTION PLANT BY FLOCCULATION

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***RINGKASAN:*** *Rawatan enapcemar karbida melalui proses pemberbukuan merupakan teknik yang agak baru yang dianggap lebih mesra alam dan ekonomik jika dibandingkan dengan rawatan kolam yang diamalkan oleh industri tempatan. Kajian dibuat dengan memasukkan 200 ppm atau 400 ppm bahan pemberbukuan pepejal atau cecair ke dalam bekas berisipadu 15,000 liter di mana campuran enapcemar / bahan pemberbukuan disuap sama ada dari bahagian atas atau bawah bekas. Untuk tujuan komersial kepekatan ataupun kealkalian enapcemar pada 25% perlu dicapai. Dalam kes ini kepekatan yang dikehendaki diperolehi dengan menambahkan 200 ppm bahan pemberbukuan cecair dari bawah bekas. Enapcemar yang terhasil mempunyai pH 12.9 sekarang sedia untuk dijual kepada industri-industri untuk peneutralkan sisa berasid. Di samping penjualan enapcemar tersebut implementasi proses pemberbukuan juga dapat mengelakkan kos timbus tanah dan pengurangan pembaziran air melalui proses kitar semula air tercemar.*

**ABSTRACT:** The treatment of carbide sludge by the flocculation process is a relatively new technique, which is considered more environmentally and economically favourable compared to a pond system commonly practiced in local industries. Tests were carried out in a 15,000 litre vessel using 200 or 400 ppm solid or liquid flocculent, with the slurry / flocculant mixture fed either from the top or bottom. The targeted sludge concentration or "alkalinity" of 25% solid, which is the value desired for commercial purposes, was most optimally achieved with 200 ppm liquid flocculant, fed from the bottom. The sludge thus formed, with a pH of 12.9 is readily purchased by other industries for neutralizing acidic wastes. In addition to the sale of sludge, implementation of the flocculation system eliminates land-filling costs and reduces water usage through the possibility of water recycling.

**KEYWORDS:** Carbide sludge, acetylene, flocculation, polymeric flocculant, sludge alkalinity

## INTRODUCTION

The production of acetylene from calcium carbide generates the by-product carbide sludge, which is mainly calcium hydroxide. The chemical equation is:

$$CaC_2\,(s) + 2H_2O\,(l) \rightarrow C_2H_2\,(g) + Ca(OH)_2\,(aq) + 64\ \text{kcal} \tag{1}$$

Generation of 2400 $m^3$ / day of acetylene consumes 900 kg of carbide, while the amount of sludge produced may exceed $10^4$ kg per day. The composition and mineral content of carbide sludge varies depending on (i) the method of carbide manufacture, (ii) purity of carbide, (iii) the rate of reaction in the generator and (iv) the type of water used (Matheson and Henzen, 1974). The moisture content of carbide sludge is 60-70%, with the concentration of calcium hydroxide ranging between 30-40%. Carbide sludge contains heavy metals such as aluminum, copper, lead, manganese, nickel, iron and boron and has a pH of 12 to 14. Table 1 shows the similarities of sludge characteristics in acetylene factories in Malaysia and abroad.

**Table 1.** Characteristics of Untreated Carbide Sludge from Acetylene Factories in Malaysia and Abroad

| Parameter | Malaysia | United Kingdom | USA |
|---|---|---|---|
| pH | 12.2 ± 0.3 | 12.3 ± 0.3 | 12.9 ± 0.3 |
| COD | 90 ± 8 | 89 ± 8 | 94 ± 8 |
| BOD | 30 ± 4 | 29 ± 4 | 31 ± 4 |
| COD:BOD | 3.0 ± 4 | 3.1 ± 4 | 2.9 ± 4 |
| Copper | 5.09 ± 0.01 | 6.01 ± 0.01 | 6.04 ± 0.01 |
| Lead | 11.10 ± 0.01 | 11.20 ± 0.01 | 11.30 ± 0.01 |
| Ferum | 48.68 ± 0.01 | 49.01 ± 0.01 | 48.90 ± 0.01 |
| Manganese | 1.97 ± 0.01 | 1.89 ± 0.01 | 1.98 ± 0.01 |
| Nickel | 3.84 ± 0.01 | 3.85 ± 0.01 | 3.79 ± 0.01 |
| Zinc | 2.49 ± 0.01 | 2.47 ± 0.01 | 2.50 ± 0.01 |

Metals in ppm

The common practice among industrial gas producers is to construct an outdoor reservoir to store sludge from the process. The carbide lime slurry is transferred from the generator into this lime or sludge pond for an interim period until final disposal. Retaining the slurry in the pond causes the hydrate solids to settle and concentrate to become a semi-solid paste (with 50% water). The water component from the slurry is lost either by evaporation, or penetration to the ground. With the increase in acetylene production over the years, however, this pond system has become very ineffective and potentially hazardous. Carbide sludge stagnated in the pond releases very strong odor. During rainy days, the sludge tends to overflow, causing messy and dirty conditions around the sludge disposal area. Sometimes it flows into nearby monsoon drains and this violates the Department of Environment (DOE) by laws, particularly since the sludge pH exceeds the DOE limit of pH 6 to 9 for effluent discharge.

There is growing awareness of the ecological implications posed by the disposal of carbide sludge into the environment. Processing the sludge by the use of vacuum filtration produces a liquid filtrate that satisfies Standard B of the DOE limits (Palanisamy *et al.*, 2000). However, there is added cost as the filter cake still requires proper disposal as scheduled waste. Other alternative methods for the sludge disposal are explored to overcome current emission regulations and economic considerations. The possibility of the sludge being utilized by other industries if the solid content is regulated or adjusted, offer an opportunity for generating additional income for the company. The sludge could be supplied either as watery slurry at 33% solids by weight or as plastic paste with 50% lime solids and 50% water. The alkaline pH of 12 to 14 could be used to neutralize acidic waste from other industries (Richard, 1985). There is no need to satisfy any emission standards when the product is sold to another industry to be used.

This work investigates the treatment of the sludge by flocculation to achieve the desired percentage of solids and alkalinity for use in neutralization. Flocculation using polyelectrolytes is widely used in mining industries and is being considered for sewage treatment (Hughes, 1989). A new type of polymeric flocculating agent has facilitated the flocculation of acetylene plants wastes in the UK (Jeffrey, 1997). The objective of this research is to investigate the applicability of this flocculent to treat acetylene sludge under Malaysian conditions and to determine an optimal condition under which to carry out the process.

## MATERIALS AND METHODS

A preliminary study on carbide sludge settling was conducted in a jar test apparatus, the Chemix Gloc Tester, Model CL6, which is equipped with mechanical stirrers, speed controller and timer. The flocculent is a high molecular weight (7.8 million) polymeric flocculating agent of anionic character. Having the trade name, "Fossi-floc" the chemical is supplied by Allied Colloids Pt. Ltd. (UK).

Following the jar tests, experiments were conducted on a larger scale of 15,000 litres. Figure 1 shows a schematic of the plant. The sludge was pumped into the settling tank from a 90,000 litres storage tank using a slurry pump model XX178, after it had been allowed to settle overnight and longer. The flocculent dosing rig used was provided by Harpers of York. The flocculent was stored upstream of pump 1. The flocculent and slurry mixes at the pipe junction connecting pumps 1 and 2, and the mixture was fed into the settling tank either:

(i) from the top of the tank through an adjustable 2 cm pipe, the exit of which was approximately four meters above the tank base, or

(ii) via a 3 cm take off valve at the bottom of the settling tank.

The flocculent dosing rate was adjusted according to the quality of the flocs in samples taken from a point 5 meters downstream from the slurry transfer pump.

A total of five experiments were carried out based on the results of the jar tests. The operating parameters are as tabulated below:

**Table 2.** Experimental Conditions

| Flocculent phase / Concentration | Feed point |
|---|---|
| Liquid / 400 ppm | Top |
| Liquid / 200 ppm | Top |
| Liquid / 200 ppm | Bottom |
| Solid / 200 ppm | Top |
| Solid / 200 ppm | Bottom |

The liquid flocculent was activated by mixing 0.4 L of the flocculent with 1,000 L of distilled water, and allowed to stand for 20 minutes. With the solid flocculent, 4 kg of the flocculent was slowly added to 500 litres of pure water, mixed and left overnight to stand.

Throughout the trials, carbide sludge samples were taken at regular intervals from the eight sample ports located on the settling tank (Figure 1) to determine the variation in lime concentration at different height and time. The total experimental time varied from run to run depending on the progress of flocculation. Sampling was ceased when the desired solids concentration was achieved, satisfactory settling of the flocs have occurred and no further significant changes were expected. The samples were taken from the top to the bottom (port 1 to port 8) and their alkalinity determined by titration with sodium hydroxide after the addition of excess hydrochloric acid to neutralize the sludge. The titration procedure and formula used to calculate the calcium hydroxide concentration are given elsewhere (Palanisamy, 1998).

Upon completion of each run, the slurry is removed from the settling tank and filtered to remove the water for recycling. The flocculated (semisolid) portion that separates from the water would maintain the 25% solids concentration.

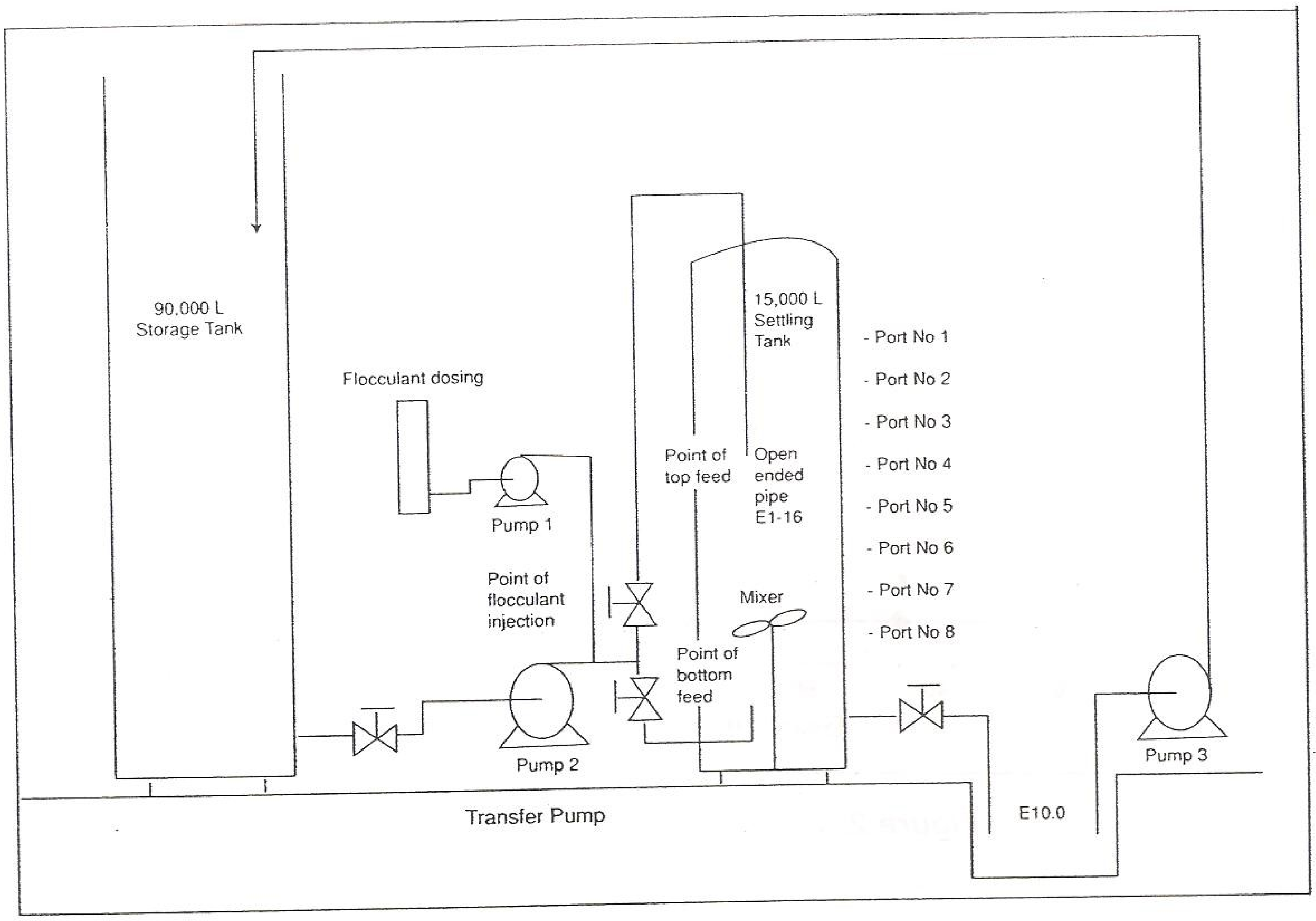


***Figure 1.*** *Schematic plant of carbide sludge flocculation unit*

## RESULTS AND DISCUSSION

Three main parameters varied in the five experimental runs were the flocculent phase (solid or liquid) and concentration, and the point of feed injection into the settling tank. In addition, the feed rate and total time of sludge concentration monitoring were varied from run to run depending on the progress of each one. The objective is to determine the most optimal condition to achieve 25% solid in the sludge. This gives the alkalinity suitable for use in acid neutralization in other industries.

Figures 2, 3, 4, 5 and 6 are plots of solid percentage as functions of time and distance from the top of the settling tank. The plots indicate the progress and final result of the flocculation process. The most optimum condition is ascertained based on these data and visual observation of the settling process and floc characteristics. In general, a high settling rate is desirable, but too rapid floc formation and settling can lead to solids concentration exceeding the desired limit.

The flocs that formed were large and the water component separated rapidly. The 400 ppm flocculent concentration was reached after 45 minutes of feeding and the mixture occupied about 10 $m^3$ in volume.

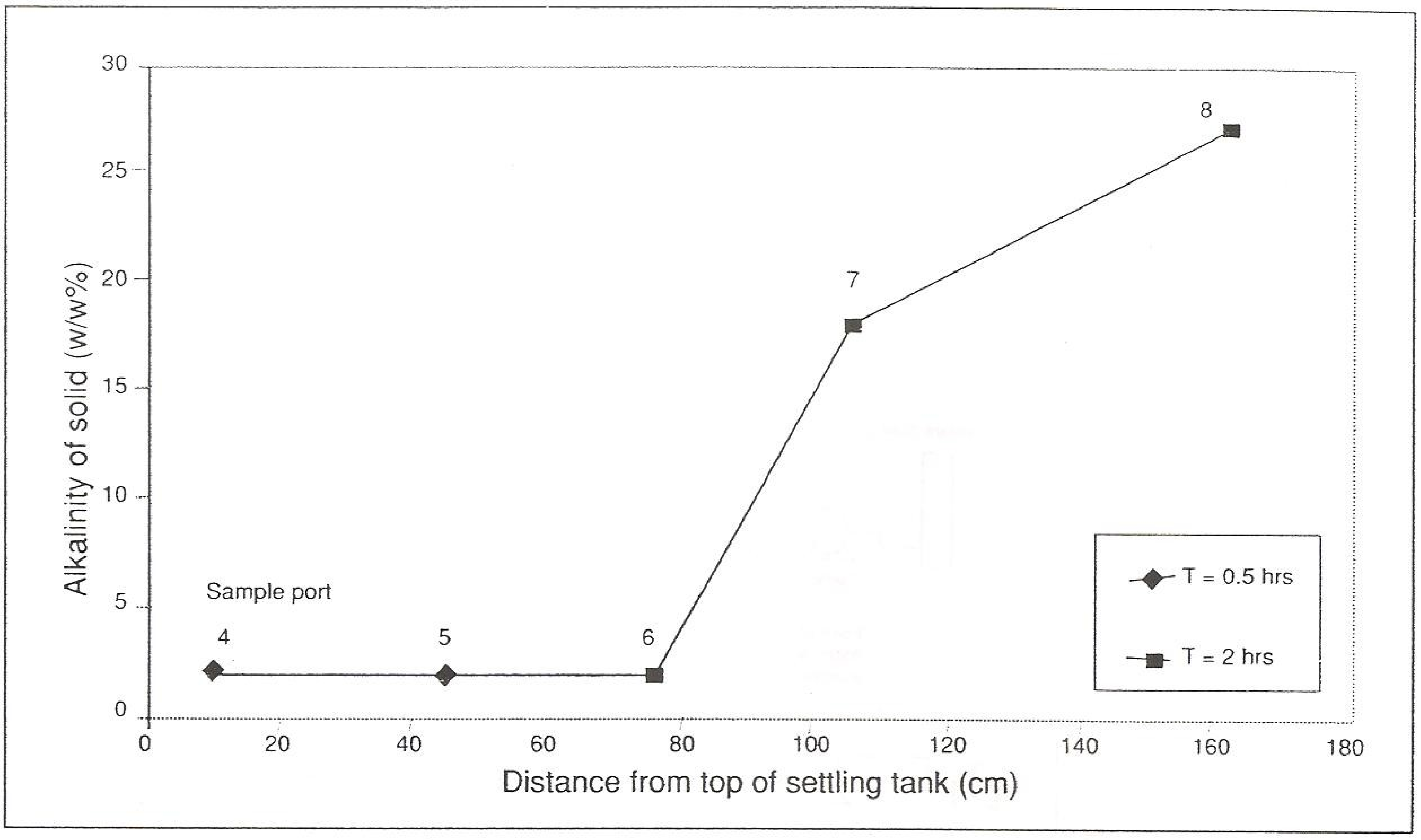


***Figure 2.*** *Liquid flocculant - 400 ppm; top feed*

Figure 2 shows a single curve going through the points of alkalinity at 5 sampling ports over a period of 2 hours. The vessel content did not reach ports 1, 2 and 3. At the levels of ports 4, 5 and 6 there was only about 2% alkalinity while ports 7 and 8 had concentrations of 18% and 26%, respectively, after 2 hours. The plot indicates high rate of settling of the flocs, corresponding to the high solids concentration at the levels of the lower ports (ports 7 & 8).

The lower flocculent concentration was achieved by reducing the dosing pump until the sample taken from the mixing point downstream of the pump was barely flocculating.

The plots in Figure 3 portray a more even distribution of flocs throughout the tank; hence a lower rate of settling compared to the 400 ppm case. After half an hour, all the ports had an average of 14% alkalinity compared to only 2% in the previous run. After 2 hours the average alkalinity had risen to about 17%, and after 6 hours it reached approximately 20%. As indicated by the values at port 1, the settling tank was filled to within 6 cm of the top of the tank in about one and half hours. Around the 8$^{th}$ hour the liquid was clear at the first two sampling ports and the slurry could be easily pumped out from the tank.

The dosing control was as with the top feed run at 200 ppm. Corresponding to the location of the bottom feed point, ports 1 and 2 which are the furthest from the feed inlet and the impeller, had less than 2% alkalinity throughout the duration of this experiment, implying that these levels were virtually cleared from the time the tank was filled. This means that

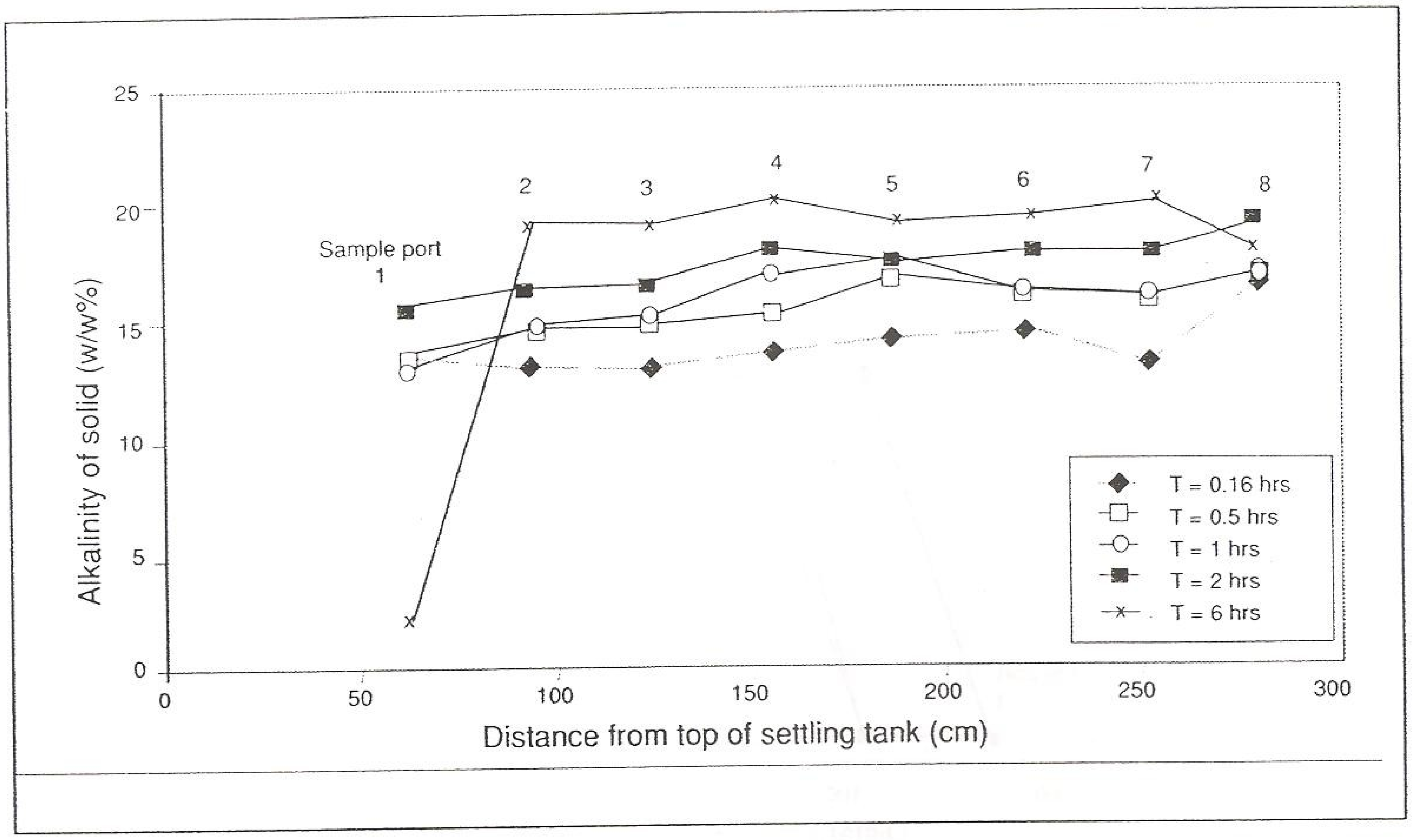


***Figure 3.*** *Liquid flocculant - 200 ppm; top feed*

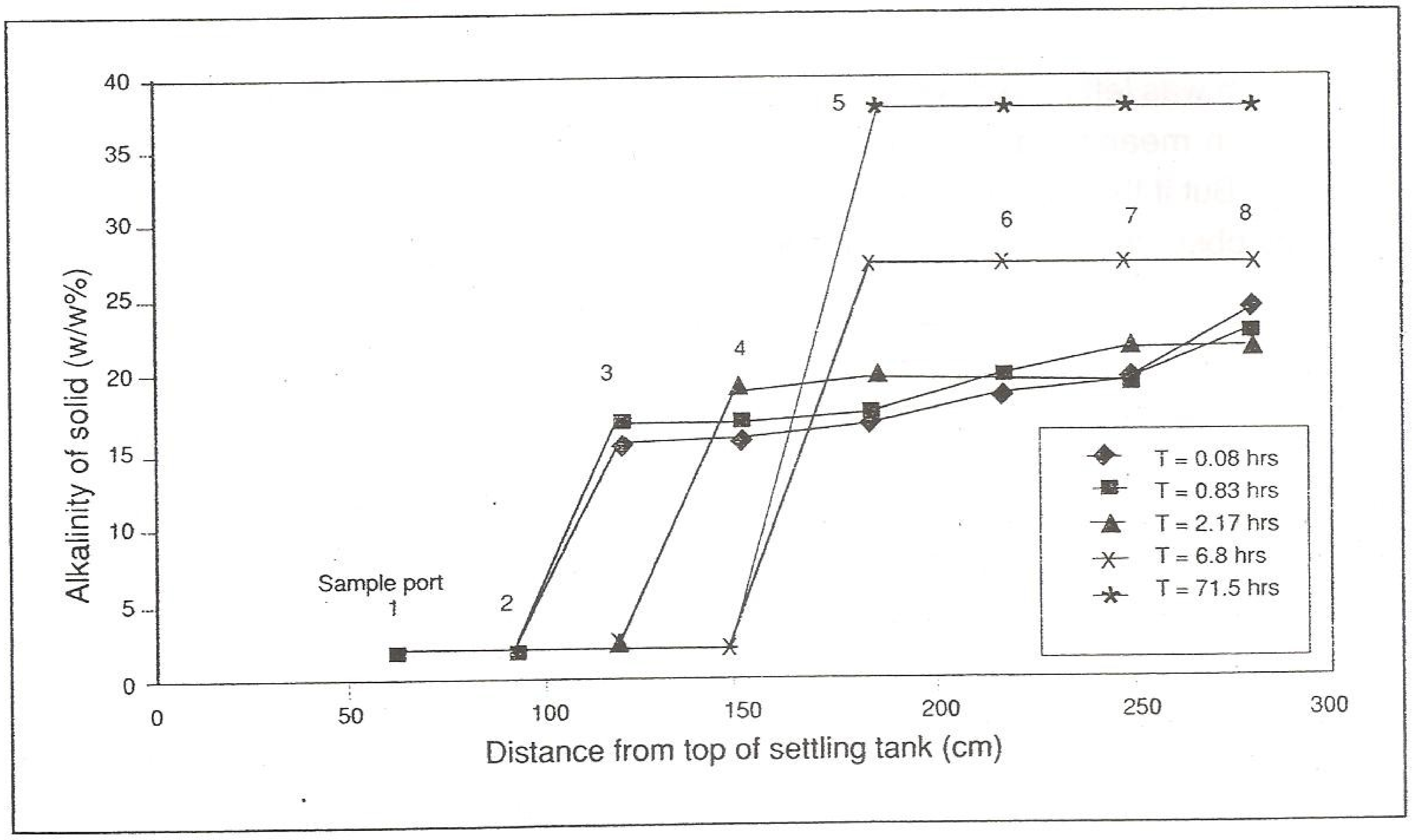


***Figure 4.*** *Liquid flocculant - 200 ppm; bottom feed*

gravitational force overrides the upward force of the slurry entering from the bottom feed point. By around the second hour, the solids in port 3 also cleared while ports 4 and 5 had an average of about 19%, ports 6, 7 and 8 reached 20%, and then increased to 26% after 6 hours.

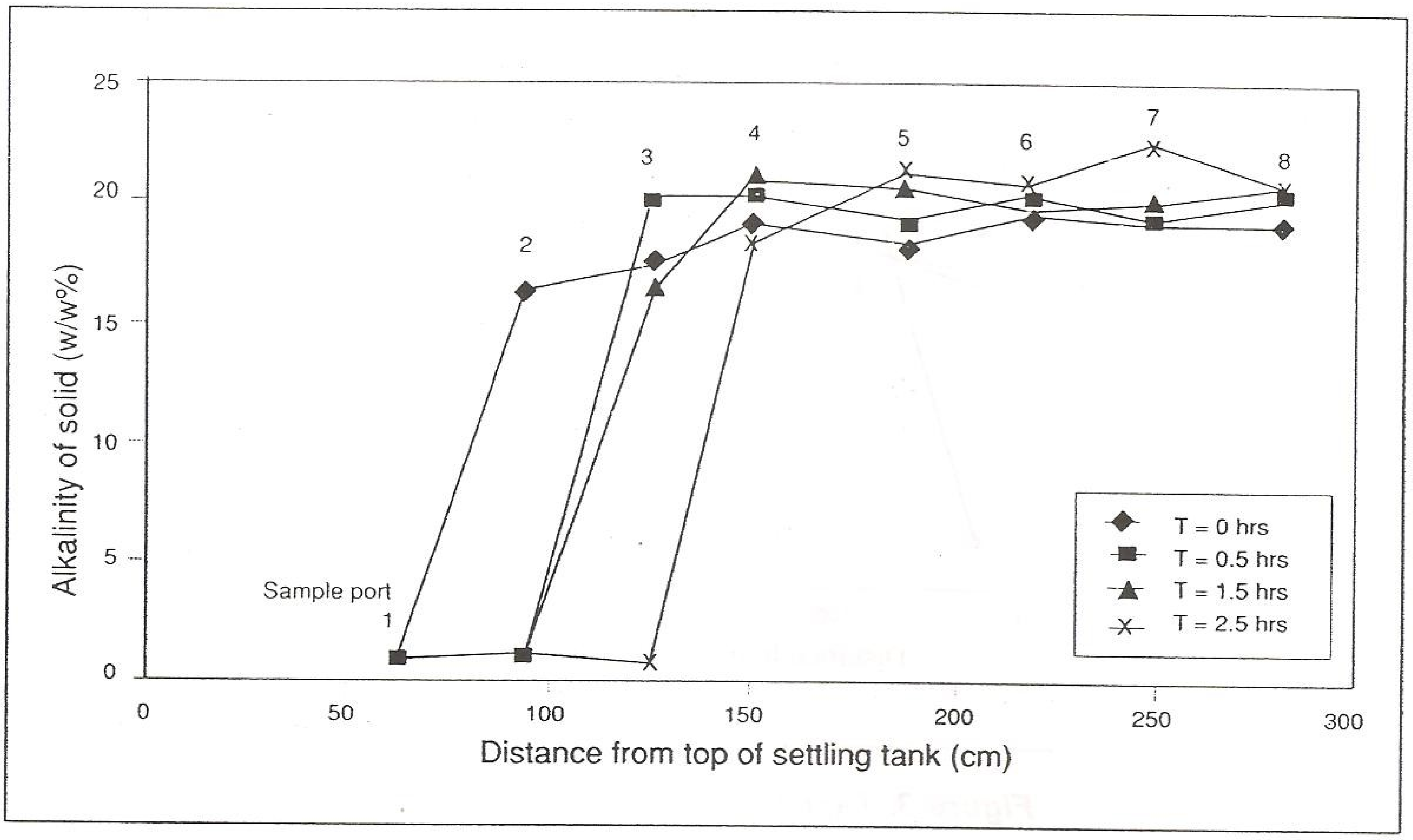


***Figure 5.** Solid flocculant - 200 ppm; top feed*

The system was left for 3 days. The alkalinity for ports 5 to 8 rose from 20% to 25% over 68 hours which means that the sludge could be removed after 68 hours and at the desired alkalinity. But if the sludge was left longer within 4 hours beyond that, a marked increase to 38% was observed for ports 5, 6, 7 and 8.

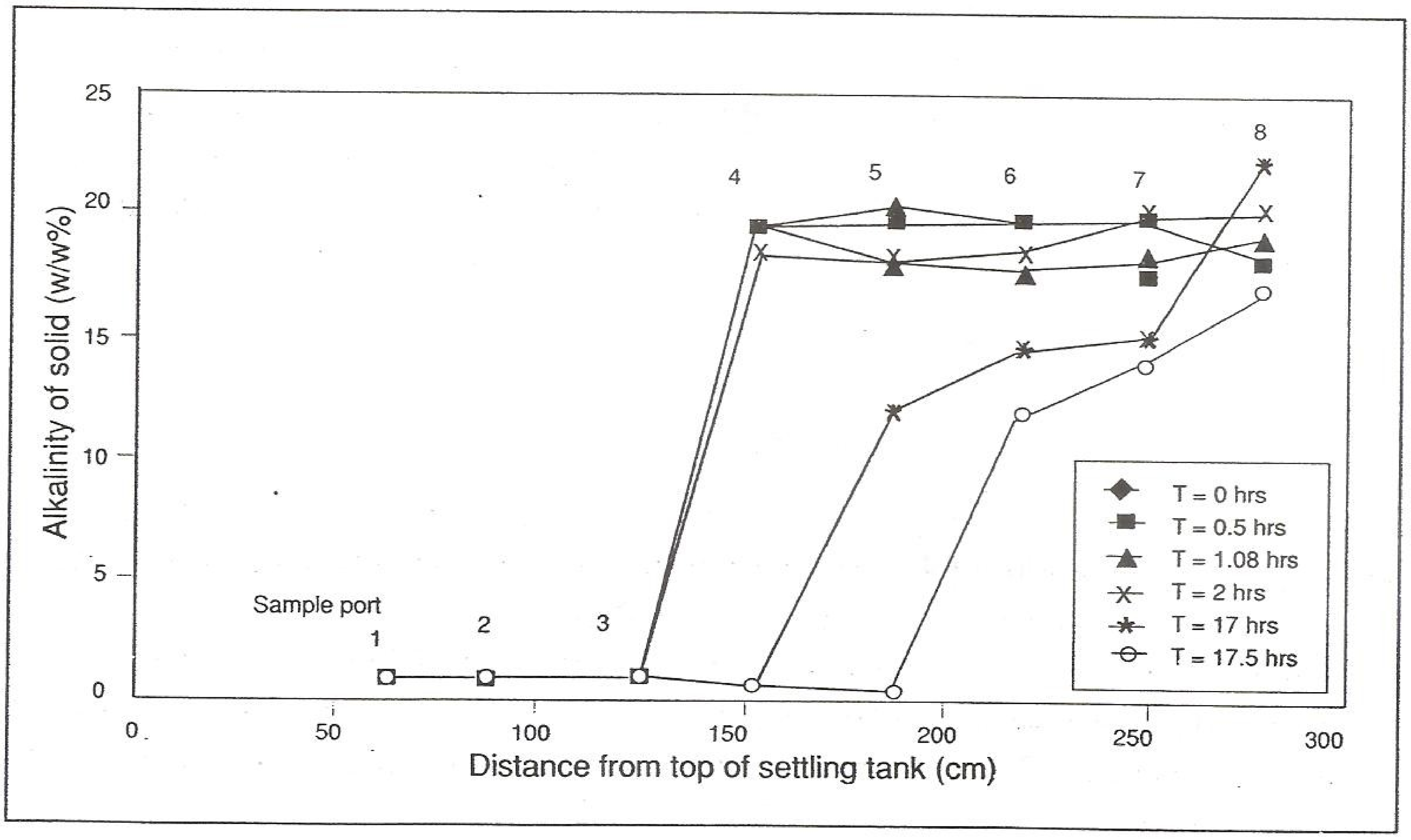


***Figure 6.** Solid flocculant - 200 ppm; bottom feed*

The floc formation rate was only slightly more than that for 200 ppm liquid flocculent top feed (Figure 3) but ports 1, 2 and 3 were cleared within 2 hours of the experiment, unlike that for the liquid flocculent where it took 6 hours for port 1 alone to clear. The alkalinity at port 1 decreased from 16% to 2% (w/w) within half an hour whereas at ports 2 and 3 the alkalinity increased (from 17% to 20%) and then decreased to 2%. Alkalinity at ports 4 to 8 remained between 20% to 21% throughout the trial.

The tank was filled in one hour, by which time the sludge at the first two sampling ports (30% of the tank, at the top) was already clear and within the next half an hour the sludge at port 3 also cleared (Figure 5). Thereafter settling became very slow, as indicated by the flat concentration profiles for ports 4 to 8 around an average of 21%.

Left overnight, the fourth port cleared. At this point it was of interest to see how the slurry changed when water was removed. Water from ports 1-4 was carefully pumped without disturbing the thickened lime. Within half an hour of removing the water, the sludge at port 5 had cleared. This explains the marked decrease in concentration for ports 5, 6 and 7 at the $17^{th}$ hour, and an increase in concentration for port 8, which later reduced to a final value of 15%. As dewatering was carried out, the alkalinity increased from 25% to 35%, the floc size increased and the slurry fluidity decreased. This could pose a problem in slurry discharge.

## ECONOMIC CONSIDERATIONS

With an investment of RM1 million (US$ 1=RM3.80) to implement the carbide sludge waste treatment and recovery facility, the company could save RM300,000 per year by using recycled water. An additional RM200,000 per year could be economized by avoiding landfill charges. Medical expenses are projected to decrease by about 20% from the current value of RM31,000 per year due to plant workers' exposure to carbide sludge vapor. The treated sludge could be sold at RM1,200 per ton and the total revenue could reach RM1 million per year. The total cost of flocculent comes to RM0.30 million per year (Figure 7).

## CONCLUSION

The study was to look at the possibility of using flocculation as a more economical and environmentally friendly method of treating carbide sludge waste from acetylene production plant. The tests were carried out using a system already implemented in the United Kingdom. The main objective was to determine the most optimum condition under which to carry out the treatment. This was based on concentration and time data, and also substantially on qualitative observation of the process characteristics. Admittedly, the main shortcoming of the experiments was the inconsistency in the duration of experimental runs. Nevertheless,

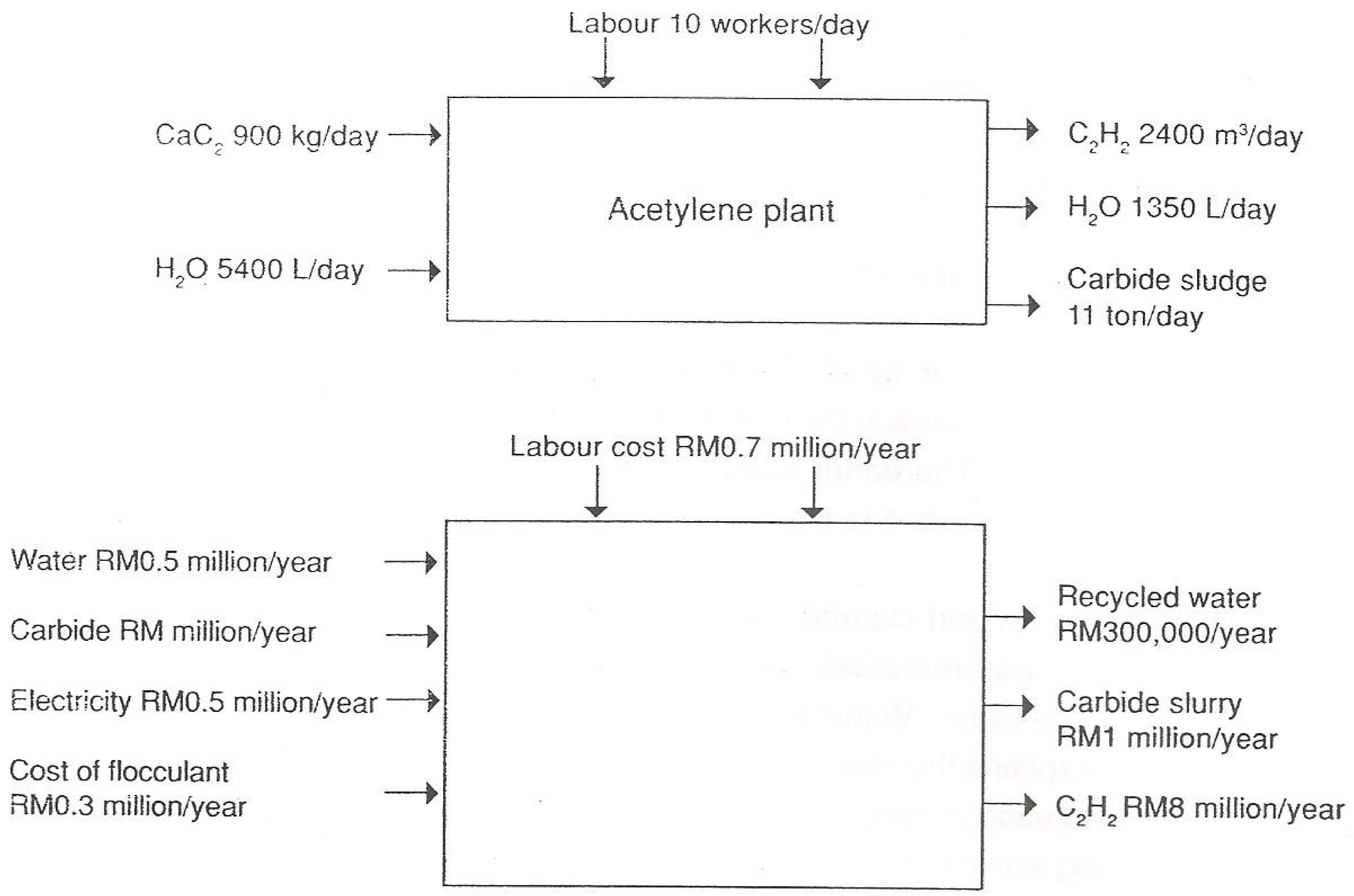


***Figure 7.*** *Flow chart showing input and output of an acetylene production plant with flocculation as the waste treatment method*

from the summary of results tabulated in Table 3, some deductions can be made as to the best likely operating condition to select. The flocculent concentration of 200 ppm may seem high, but this was considered necessary, as the sludge has to withstand high pumping stresses during transfer from tank to tank.

In general, the solid concentration reached around 20% after about 2 hours; and reasonable settling occurred for all cases. The 200 ppm liquid flocculent, bottom fed was selected as the recommended condition under which to operate because of better settling rate, and the flocs were stable even after removal of water. This was important for transfer and handling after the flocculation process.

This study has shown the possibility of using flocculation to treat carbide sludge for further use in another local industry. Since this method eliminates the need to meet emission standards, and can generate income for the particuiar company that produces the sludge, it offers an attractive alternative method of sludge disposal. The method also has potential for application on other types of sludge.

**Table 3.** Summary of Experimental Results

| Operating conditions | Observations | Comments |
|---|---|---|
| 400 ppm LF, Top feed | • Settling rate too high<br>• Flocs too large<br>• Final concentration after 2 hours at port 8 exceeds 25% | Overdosed |
| 200 ppm LF, Top feed | • Low settling rate (concentration >10% for all ports)<br>• Only port 1 cleared after 2 hours<br>• Final concentration after 6 hours about 19% for ports 2-8 | Low settling rate |
| 200 ppm SF, Top feed | • Settling rate better than liquid flocculant<br>• Ports 1, 2, 3 cleared after 2.5 hours<br>• Final concentration after 2 hours is about 22% at ports 5, 6, 7 and 8. | Slightly better than liquid flocculant in terms of settling. |
| 200 ppm SF, Bottom feed | • High settling rate<br>• Ports 1, 2, 3 clear almost throughout experiment<br>• Average value around 20% at ports 4-8, but dropped overnight<br>• Sudden increase in concentration beyond the 25% criterion after water was removed. Floc size increased and fluidity decreased. | Some instability upon water removal. Perhaps need longer time for settling before water removal. |
| 200 ppm LF, Bottom feed | • Ports 1, 2, 3 cleared after 2 hours<br>• Ports 4-8 had average concentration of 20% after 2 hours<br>• After 3 days 25% criterion was met, but if left till the 70th hour concentration increased to 35%.<br>• No further settling occurred after water removal. | Better stability than with solid flocculant bottom need. Best option of the 5 cases. |

LF = Liquid Flocculant
SF = Solid Flocculant

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